

## FIELD IONIZATION MASS SPECTROMETRY FOR CHARACTERIZING COALS AND COAL-DERIVED LIQUIDS

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### INTRODUCTION

The fossil fuel research program at SRI International has greatly benefited from the availability of on-site FIMS capability. In this paper we present a potpourri of FIMS applications from various aspects of coal research to demonstrate the technique's versatility. These applications include (a) differentiating coal types (b) analyzing coal tars, (c) determining the fate of a nitrogen-containing donor solvent in coal liquefaction, (d) identifying species responsible for catalyst deactivation, and (e) understanding why certain liquefaction resids are more difficult to upgrade. This list includes examples of characterization of individual species from peak intensities, which is possible in certain instances, and the use of overall FIMS profiles to identify trends in a series of samples.

### EXPERIMENTAL

The technique of field ionization (FI) consists of passing the vapors of a material through a region of intense electric field to polarize and ultimately ionize the molecules. The ions are then mass analyzed using standard mass spectrometric techniques. For most organic compounds, this procedure causes minimal fragmentation and produces only the molecular ions. (1) Thus, complications arising from fragmentation during ionization are minimized. Another advantage of field ionization is that the relative field ionization efficiencies of various hydrocarbon types are within a factor of two of alkyl aromatics except for saturated acyclic hydrocarbons, which ionize about a third as efficiently. For many other ionization techniques, such as field desorption, low-voltage electron impact, secondary ion mass spectrometry (SIMS), or fast-atom bombardment (FAB), the relative ionization efficiencies can differ by more than one or two orders of magnitude. Thus, even without any corrections for sensitivity, the FI mass spectra represent the true molecular weight profile fairly accurately. This is particularly useful in complex unknowns where extensive calibration is not feasible. It should be noted that practical advantage can be taken of this similarity in ionization efficiency *only* if appropriate technique and care is used in preparing and operating the tantalum foil ion sources that are used at SRI.

SRI's FIMS instrument consists of a foil-type field ionizer interfaced with a 60-degree magnetic-sector mass analyzer and a PDP 11/23 computer for instrument control, data acquisition, and report production, as previously described.(2) The spectrometer has a resolving power ( $M/\Delta M$ ) of 1300, although it is capable of scanning up to 3000 Da. The sample is weighed into a melting point capillary and introduced into the spectrometer with a heatable direct insertion probe. It is heated at a fixed rate from ambient (or  $\sim 67^\circ\text{C}$  for samples with sufficiently high vapor pressure) to about  $700^\circ\text{C}$ . The spectra of the evolving volatiles are continuously recorded, and at the end of a run, they are added to produce a "sum" spectrum of the total volatiles. The capillary is weighed afterward to determine the percent volatilization.

The sum spectra consist of (a) intact molecular ions from individual chemical species originally present in the sample, (b) ions produced from any ion fragmentation that may occur, and (c) molecular ions of fragments that are generated thermally during the ramped heating. The ion fragments are most often totally negligible, as asserted above, but the thermal fragments can be substantial, depending on the volatility and reactivity of the sample. However, in both cases, the manner of presentation of the spectral intensities can generally indicate the extent to which (b) and (c) contribute. Since ion fragments will accumulate at the masses corresponding to the common stable positive ions, the typical absence of significant intensity at, for example,  $m/z$  57 (where the

easily generated t-butyl ion fragment appears) indicates that the percent fragmentation at each of the other hundreds of masses that may have had attached t-butyl fragments must have been very small indeed. For cases where there is significant formation of volatiles through thermal decomposition in the heated source, this is usually revealed by the appearance of some smaller ions as the source is progressively heated. Contributions from pyrolysis during heating are of course significant for heavy coal conversion fractions such as preasphaltenes and vacuum resids. These pyrolytically generated volatiles, when recognized, can sometimes provide valuable information.

## RESULTS AND DISCUSSION

### 1. Differentiating Coals

We analyzed the eight coal samples from the Argonne Premium Coal Sample Program (APCSP) by programmed temperature pyrolysis directly in the inlet of the field ionization mass spectrometer.(3) The spectra of the evolved tars, but not of gases such as CO, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O, were obtained. From these data we could identify several salient rank-dependent trends. Some of these trends are known from other studies, but FIMS provides an easy means for quantifying them and developing indices that could be used in modeling. In general, the spectra appear to be composed of two groups of peaks: (a) a cluster of peaks in the low molecular weight range corresponding to homologous series of phenols and dihydric phenols and (b) a broad, roughly Gaussian, distribution of peaks spanning the mass range of 150 to 1000 Da.

The low molecular weight cluster is particularly dominant in the Beulah Zap lignite and the Wyodak subbituminous coal, as shown in Figure 1. With increasing rank, the prominence of this cluster decreases relative to the broad Gaussian envelope, whose mean appears to shift to higher masses with increasing rank. Furthermore, the ratio of monohydric to dihydric phenols generally increases with rank. A detailed examination of the broad envelope revealed the buildup of polycyclic aromatic structures in the higher rank coals. Thus molecular species with five and more aromatic rings were discernible in the spectra of the Upper Freeport and Pocahontas coals. The observed periodicity revealed homologation via both benzolog formation ( $\Delta m/z = 50$  as in naphthalene to phenanthrene and  $\Delta m/z = 24$  as in phenanthrene to pyrene) and also in the formation of biaryl linkages (most noticeably in the formation of naphthyl substituted aromatics with a  $\Delta m/z = 126$ ). (3) The shift toward higher molecular weight and away from phenolic fragments with increasing coal rank is entirely consistent with the previously articulated view (4) that low-rank, high-oxygen coals are more crosslinked to begin with and/or become so during heating, such that the molecular weight between crosslinks is small and primarily small fragments are released. These observations parallel some of those recently reported by Schulten and coworkers.(5)

### 2. Characterizing Coal Liquids

Chemical analysis of coal- or petroleum-derived liquids as well is best accomplished by first fractionating the oil into different compound classes by HPLC and then subjecting these fractions to FIMS analysis. The most evident feature in these spectra is a 14-Da periodicity arising from the various alkyl-substitution homologous series. The HPLC-FIMS approach has been used by many investigators to follow the chemical changes that accompany processing.(6-10) In general, severe processing leads to dealkylation and formation of larger PAH structures. The net result is a simplification of the FI-mass spectra, which show an increasing dominance of a 50-Da periodicity instead of the more common 14-Da periodicity. An extreme of this behavior can be seen in high-temperature coal tars, which can consist almost exclusively of dealkylated aromatics, as shown in Figure 2.(7)

### 3. Fate of Amine Solvents during Coal Liquefaction

We examined liquefaction products obtained with and without 1,2,3,4-tetrahydroquinoline (THQ) as a solvent component to determine the fate of THQ.(8) At the time this study was undertaken, it was well recognized that (a) use of THQ dramatically increased coal conversion to soluble products, but these products were much less distillable than the normal toluene solubles, and (b) a

substantial portion of the THQ was not recovered from the solvent. The nitrogen content of the resid produced in batch autoclave liquefaction was significantly greater than without THQ. It was postulated that THQ was adducted into the resid by means of H-bonds that limited its recovery in the normal fashion, but that some physical or simple chemical separation would still make THQ available under recycle conditions.

FIMS of the resid showed a complete absence of a peak at 133 Da corresponding to THQ. Since even the strongest of hydrogen bonds would provide only a vanishingly small degree of association at the high vacuum field ionization condition, this observation provided incontrovertible evidence that THQ was not lost merely by H-bonding. FIMS also showed that after correcting for natural  $^{13}\text{C}$ -content, the profile of the odd masses was significantly more intense for the resid obtained with THQ as a solvent component, as shown in Figure 3. The increase in the intensity of the entire odd-mass envelope indicated that THQ was incorporated by covalent linkages into a whole host of resid components, and is hence, for all practical purposes, irretrievably lost to the resid. FIMS and GC-MS analysis of the lighter fractions showed many specific coupling products, thereby providing insight into the types of reactions contributing to THQ loss.

#### 4. Resid Reactivity

In a recent study (11,12) we analyzed fifteen recycle resids from five runs conducted at the Wilsonville facility to help address the question of what structural and process factors help make some resids much more convertible than others. At first glance, the spectra looked very similar with only a broad, featureless envelope. Closer examination, however, revealed that the mass spectra consistently showed the same set of a few prominent peaks in the low mass end, where the distillate-resid cut had sent lower boiling components (i.e., aliphatics) of similar molecular weights into the distillate fraction. Some of these prominent peaks are identified in Figure 4. Interestingly, these prominent masses left in the resid were identical to those previously identified by Sullivan et al. and associated (10) with increased difficulties in hydrotreating vacuum gas oils derived from petroleum resids. This coincidence is remarkable and we believe that a quantitative analysis could lead to an index of resid reactivity and help as well to understand the kinetic factors that control the ring-growth processes.

Apart from information contained in these few specific peaks, we can also derive useful information from overall FIMS profiles. Many of the liquefaction resid samples exhibited a bimodal molecular weight distribution. The relative amounts of the low and high molecular weight components differ significantly from sample to sample, and a simple mathematical deconvolution into Components A and B revealed a correlation between the variations in A and B on the one hand and coal type, process conditions, and process performance on the other. The deconvolution led to several conclusions reasonably in concert with what is already recognized in coal liquefaction. For example, this analysis clearly showed the occurrence of retrograde reactions after the second-stage reactor, while the oil was held at temperature and handled through the ROSE-SR unit.(13) This retrogression was evidenced by an increase in the amount of component B. It was satisfying to see this and other observations about reactivity reiterated, not on the basis of yields, but on the basis of differences in molecular weight distribution, when the streams are already constrained by process conditions and product fractionation to be as similar as possible.

#### 5. Catalyst Fouling

In order to determine the types of compounds that strongly adsorb on supported liquefaction catalysts and likely deactivate them, we used FIMS to characterize the carbonaceous deposits on the spent catalysts from DOE's Wilsonville facility.(14) The spent catalyst extrudates (Ni/Mo on alumina) were washed with tetrahydrofuran (THF) to remove any weakly adsorbed oil, and only tenaciously held materials remained. The washed extrudates were analyzed by heating a single pellet in the direct insertion probe of the mass spectrometer, and the evolved volatiles were then field ionized to produce the molecular ions. The spectra appeared very much like that in Figure 2 above, except that they are dominated not by PAH, but by the corresponding azaaromatics and their alkylated derivatives. These basic compounds are expected to adsorb strongly to alumina and

may have indeed caused the deactivation. Peaks due to some purely hydrocarbon structures such as alkyl pyrenes and perylenes were also present, albeit at lower intensity than the azoaramatics.

## CONCLUSIONS

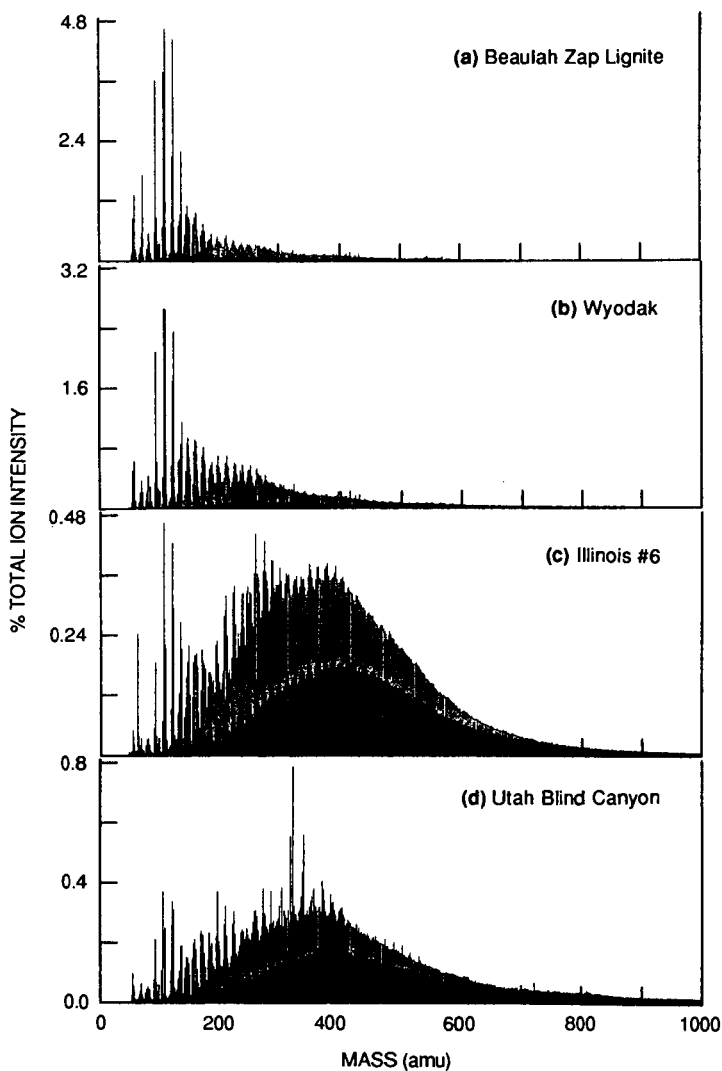
Field ionization mass spectrometry, through definitely not a panacea, has been very useful in a wide range of fossil-fuel-related research. The vapor pressure requirements for desorption/ionization under FIMS conditions definitely constitute a limitation relative to methods such as field desorption and fast atom bombardment. However, with FIMS the extent of fragmentation is often much lower than one typically observes in FAB spectra. Furthermore, the variation in substrate sensitivity is usually much less for FIMS, providing a reasonably accurate quantitative analysis without the necessity for calibration.

When field ionization is coupled with mass analysis at nominal mass resolution, it is of course often not strictly able to provide definitive molecular formula identification, let alone structural identification. However, observation of homologous series, together with any knowledge of the structural types present in the product mixture and the results of previous compound-class separation/FIMS analyses, often provide very good "provisional" identification of the structures at various masses. Furthermore, for very complex mixtures, the absence of discrimination between structural isomers can collapse hopelessly complex spectra to provide useful analyses. (For instance, considering that there are 15 different isomers among the dimethylpyrenes alone, it will generally be very useful, even in systems much simpler than coal liquefaction products, to have these isomers grouped together at  $m/z$  230.) In the examples reviewed above, a complete separation of structural and geometric isomers, such as could be provided in principle by a chromatography-MS technique, would have presented severe problems in data-handling and chemical correlation and provided little, if any, net benefit. In summary, we find that field ionization mass spectrometry, coupled with judicious use of prior separation techniques, can provide useful information on the extremely complex mixtures that constitute coal liquefaction fractions.

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Figure 1. FI-Mass spectra of the four lower rank coals from the Argonne Premium Coal Sample Program.

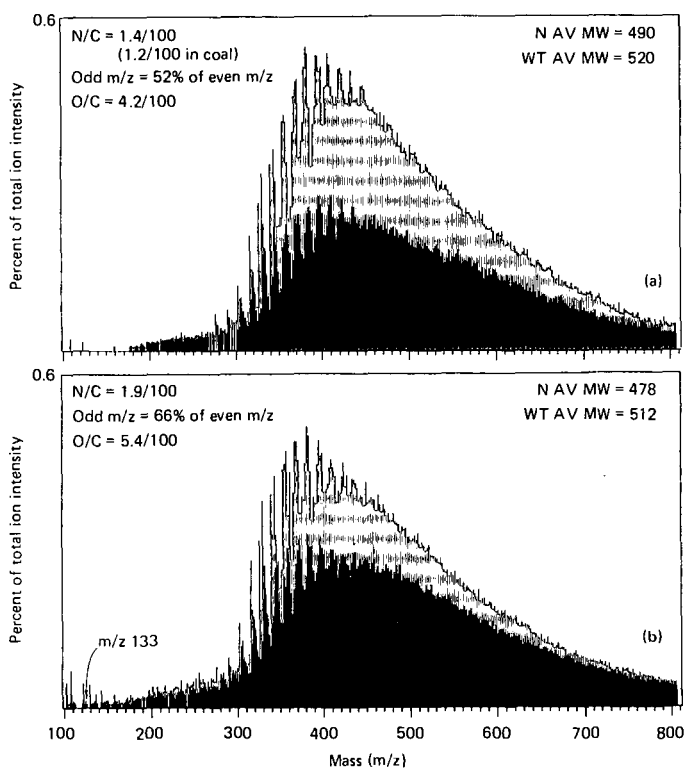


Figure 3. FI-Mass Spectrum Showing Increased Intensity of Odd Masses When THQ is Used in Liquefaction Solvent.

- (a) 1090° F+ residue, without THQ in liquefaction solvent for Wyodak coal.
- (b) 090° F+ residue obtained with 16% THQ in liquefaction solvent. Spectra in this figure are corrected for  $^{13}\text{C}$  contributions to odd masses on the basis of an average 86 wt% carbon.

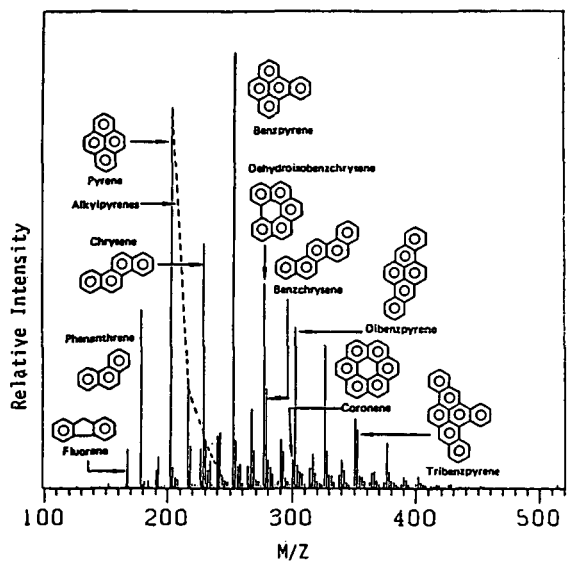


Figure 2. FI-Mass Spectrum of PCAH Fraction from Coal Tar

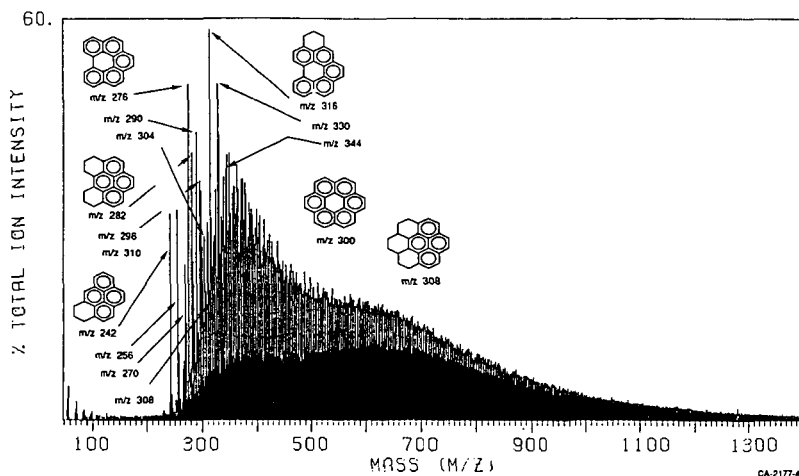


Figure 4. FI-Mass Spectrum of the 850°F+ Recycle Oil from Pittsburgh Coal (Wilsonville Run 259) Showing the Prominent PCAH Structures in the 200-350 Da Range.